

with petroleum ether (b. p. 30–60°), a pure product was obtained in the form of long stout needles: yield 50 mg., m. p. 54–56°,  $[\alpha]^{20}_D$  95.5° (0.0330 g. of substance, 3 cc. of water solution, 2-dm. semi-micro tube, 2.10° rotation to the left). The crystals were very hygroscopic and did not reduce Fehling's solution. Before analysis the substance was kept over phosphorus pentoxide in a desiccator for three days.

*Anal.* Calcd. for  $C_8H_{16}O_6$ : C, 50.0; H, 8.33. Found: C, 49.4; H, 8.6.

**Preparation of *l*-Rhamnose Dimethyl Acetal.**—A mixture of 5.4 g. of *l*-rhamnose ethylmercaptal, 10.8 g. of mercuric chloride (2 moles), 5 g. of yellow mercuric oxide and 3 g. of drierite was shaken in 60 cc. of absolute methyl alcohol at 25° for four hours, and worked up as in the above experiment. The sirup, rotating –35° in water solution, on evaporation from ethyl acetate solution became partly crystalline.

From a solution of 15 cc. of dry ethyl acetate in the ice box 300 mg. of crystals was deposited, and after one recrystallization from 15 cc. of dry ethyl acetate at 0°, 200 mg. of pure crystals was obtained: yield 5%; m. p. 123–124°;  $[\alpha]^{20}_D$  10.2° (0.1070 g. substance, 3 cc. of solution, 2-dm. semi-micro tube, rotation 0.73° to the right). The crystals are long fine needles, are not hygroscopic and

do not reduce Fehling's solution. They are easily hydrolyzed by 0.01 *N* hydrochloric acid at 100° in a few minutes.

*Anal.* Calcd. for  $C_8H_{16}O_6$ : C, 45.7; H, 8.57. Found: C, 45.8; H, 8.5.

### Summary

$\alpha$ -Ethyl *l*-rhamnofuranoside has been isolated in crystalline form from the reaction of ethyl mercaptal with mercuric chloride in neutral ethyl alcoholic solution. The pure crystals have a specific rotation of –95.5° in water solution and melt at 54–56°. They are hygroscopic and do not reduce Fehling's solution.

*l*-Rhamnose dimethyl acetal has been isolated in crystalline form by a similar reaction of the ethyl mercaptal in methyl alcohol. The pure crystals have a specific rotation of 10.2° in water solution and melt at 123–124°. This is the first observed case of direct formation of an acetal from a sugar without blocking the hydroxyl groups to prevent glycoside formation.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION]

## The Influence of Substances on the Optical Rotation of Gelatin. VII. Rotatory Dispersion of Gelatin in Urea Solutions<sup>1</sup>

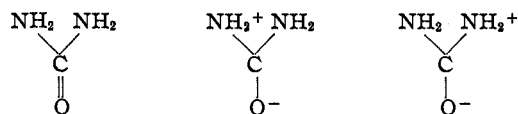
BY D. C. CARPENTER AND F. E. LOVELACE

The rotatory dispersion of gelatin–sodium halide systems follows a single-term Drude equation  $[a]_{\lambda} = k/(\lambda^2 - \lambda_0^2)$  in which  $\lambda_0$  is the position of an absorption band at 2200 Å. The effect of the halides of sodium on the rotatory dispersion constant of gelatin has been shown<sup>2</sup> to follow a linear equation with reference to salt concentration at 40°, and at 0.5° to be the result of two effects, one linear with respect to salt concentration and the other related to salt concentration by the equation

$$a/(1 - a) = e^{kC/K^h}$$

In connection with the foregoing studies of the optical behavior of protein ions in the presence of highly ionized inorganic salts, it appeared that similar studies with an optically inactive organic dipole ion would be desirable. From measurements of the dielectric constant of urea solutions<sup>3</sup>

it has been inferred that urea exists in solution as the dipole ion  $\cdot\cdot\text{NH}_2\text{C}(=\text{NH})\text{O}^-$ . The dielectric constant data, however, may be accounted for by the resonance formula



as well as the zwitter ion formula. It is common knowledge that the presence of urea brings about the "denaturation" of many proteins. Only recently have the effects of urea on proteins been followed in the ultracentrifuge. Watson, Arrhenius and Williams<sup>4</sup> reported that the molecular weight of zein was not affected by urea. Williams and Watson<sup>5</sup> believe that the action of urea on egg albumin is that of dissociation, the molecular weight of the pieces being of the order of one-half that of the original protein molecule. On dialyzing out the urea from their solutions about

(1) Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 275.

(2) Carpenter and Lovelace, *THIS JOURNAL*, **57**, 2342 (1935); **58**, 2438 (1936); **59**, 2213 (1937); Carpenter, *Cold Spring Harbor Symposia*, **6**, in press (1938).

(3) Devoto, *Atti soc. ital. progresso. sci.*, **19**, 2, 167 (1931).

(4) Watson, Arrhenius and Williams, *Nature*, **137**, 322 (1936).

(5) Williams and Watson, *ibid.*, **139**, 506 (1937).

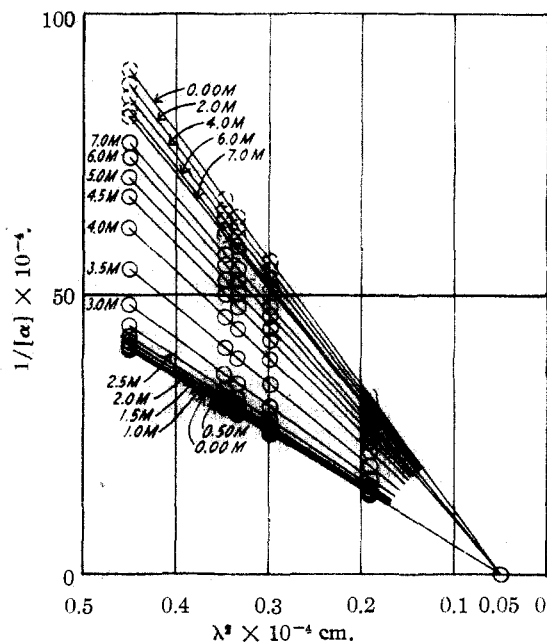


Fig. 1.—Graph of reciprocal of specific rotation *versus* wave length squared at 0.5 and 40°: ○, 40°; ◐, 0.5°.

three-fourths of the egg albumin coagulated and separated out. The protein remaining in solution after dialysis had for the most part the normal molecular weight of unchanged egg albumin, although it was not entirely homogeneous. If these authors calculated the sedimentation constant of the urea-treated protein from their Fig. 2, their reported sedimentation value is too low; however, inasmuch as assumptions of greater consequence also enter into their calculations, we will not comment further on their results.

Steinhardt<sup>6</sup> has shown a clear-cut case of the dissociation of isoelectric horse hemoglobin into half-molecules by urea. On dialysis, part of the urea treated material re-formed molecules of the original molecular weight but a large portion aggregated into still larger particles. Steinhardt concluded that pepsin was not changed materially by urea. His data actually indicate approximately a 10% increase in the sedimentation constant (much greater than the usual experimental error) indicating partial association of pepsin rather than any dissociation. The diffusion was not measured, however, in the experiments with pepsin and the molecular weight cannot be calculated without making assumptions that are often misleading.

Dissociation and denaturation of proteins by urea are clearly different processes and take

(6) Steinhardt, *J. Biol. Chem.*, **123**, 543 (1938).

place at different rates. It appears that the former occurs rapidly and the latter more slowly. Many different environmental conditions cause changes in proteins and different observers noting such changes have spoken of them rather loosely under the term "denaturation," not necessarily meaning, for instance, that the actual change produced by heat was like that effected by light, etc. It appears that in the presence of urea some proteins are dissociated and others are not. It is chiefly when one starts to remove the urea that denaturation takes place or at least makes itself obvious. The denaturation by urea seems to reside in the reuniting of the dissociated pieces in other ways than that in which they existed in the original protein. In spite of the information about protein structure obtained from X-ray work, it is not clear what holds the parallel peptide chains together in the layer level nor what forces hold together the layer-layer levels of the molecule.

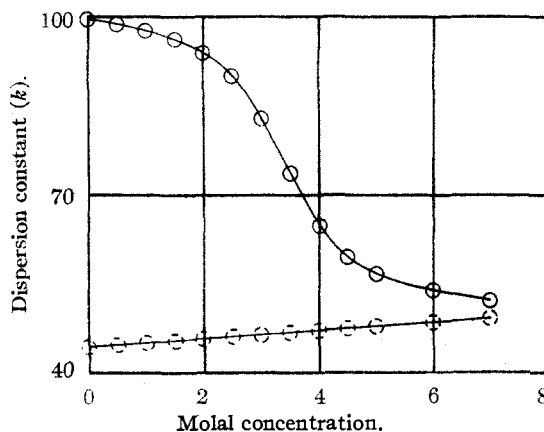


Fig. 2.—Rotatory dispersion constant of gelatin in urea solutions at 0.5 and 40°.

It is somewhat doubtful if dissociation can occur in the dimension at right angles to the main direction of the peptide chains, as dissociation of the molecule into two pieces would involve the simultaneous breakage of the peptide linkage in some forty places. Division of the molecule along the dimension parallel to the main direction of the peptide chains would cut through at least forty force fields between adjacent NH and CO groups in adjacent peptide chains. On the whole it seems more likely that cleavage of the molecule along a plane parallel to the layer levels would be accomplished by the minimum expenditure of energy. The layer-layer levels have been postulated as held together by (a)

compound formation between side-chain amino groups of the diamino acids and side-chain carboxyl groups of the dicarboxy acids<sup>7</sup> under which view the union necessarily would be between arginine and glutamic acid and would give a calculated layer-layer distance of 10.42 Å. or by (b) hydrogen-bond unions<sup>8</sup> which would give a calculated layer-layer distance of 9.94 Å. According to Astbury<sup>9</sup> the layer-layer distance of most proteins is about 10 Å. Egg albumin with equilateral dimensions of about 44 Å. may be expected to have four layer levels. Why urea dissociates egg albumin into half molecules instead of quarter molecules, if the cleavage is parallel to the layer level, is not apparent.

In the present paper we have studied the effect of urea on the rotatory dispersion of gelatin at 0.5 and 40° and have found that the same general formulas hold for its behavior as we have found for inorganic salts. After dialyzing out the urea from our most concentrated solutions we have found that the gelatin regained its original optical activity. This seems to be clear-cut evidence that in spite of the fact that many other proteins may suffer permanent "denaturation" in urea solutions, gelatin is not affected permanently by such treatment.

### Experimental

The procedure for preparing the solutions and for the measurement of rotations, density, pH, etc., was the same as has been described before. The urea was recrystallized three times from hot water and melted at 132.6° (corr). It was dried by suction and stored over phosphorus pentoxide at room temperature. In preparing solutions, due to the tremendous negative heat of solution of urea, the urea was added in small quantities to the flask of gelatin solution, warming after each addition by immersing in a water-bath at 40° and shaking gently until solution took place.

The specific rotation of gelatin in various concentrations of urea solution was measured at 0.5 and 40° for five different wave lengths of light in the visible spectrum, *viz.*: red lithium line  $\lambda = 6707.86$  Å.; sodium D line  $\lambda = 5892.62$  Å. (optical mean); yellow mercury,  $\lambda = 5780.13$  Å.

(7) Lloyd, Marriott and Pleass, *Trans. Faraday Soc.*, **29**, 554 (1933).

(8) Mirsky and Pauling, *Proc. Nat. Acad. Sci.*, **22**, 439 (1936).

(9) Astbury and Street, *Phil. Trans. Roy. Soc.*, **A230**, 75 (1931); Astbury and Woods, *ibid.*, **A232**, 333 (1933); Astbury and Sisson, *Proc. Roy. Soc. (London)*, **A150**, 533 (1935); Astbury and Lomas, *J. Chem. Soc.*, 846 (1935); Astbury, Dickinson and Bailey, *Biochem. J.*, **29**, 2351 (1935); Astbury and Atkin, *Nature*, **132**, 348 (1933).

(optical mean); green mercury,  $\lambda = 5460.73$  Å.; and the deep blue mercury line,  $\lambda = 4358.34$  Å. The light filters employed have been described. The gelatin concentration of the various solutions was 0.7641 g. per 100 g. of solution.

### Discussion and Conclusions

In Tables I and II are recorded our data taken at 0.5 and 40°, respectively, for the five wave lengths employed. In Fig. 1, these data are graphed, plotting the reciprocal of the specific rotation against the square of the wave length at which the respective rotations were measured. The relationship is linear, the same as we have recorded for the effect of the various halides of sodium, which means that a single-term Drude equation expresses the results.

The straight lines in the graph for urea cut the  $x$ -axis at  $\lambda_0 = 2200$  Å. the same as for the halides. This means that the absorption band controlling the dispersion of gelatin is located at 2200 Å. The same value for  $\lambda_0$  was obtained by mathematical solution of our data as has been done before. The values of  $k$ , numerator in the Drude equation, were calculated for each urea concentration and appear in Table III and are graphed in Fig. 2. At 40° the  $k$  values bear an essentially linear relation to concentration of urea as given by the equation

$$K_{40^\circ} = 44.517 + 0.6138 C_{\text{urea}} \quad (1)$$

There is a tendency for the factor preceding the concentration term to increase slightly with increasing urea concentration, but for the purposes of this paper an average of these factors may just as well be used. For the first time in our experience with the effect of added substances on the rotation of gelatin, the added substance increases the dispersion constant at 40° as its concentration is increased. For all of the substances we have examined previously the dispersion constant has decreased at all temperatures with increasing concentration of the optically inactive substance. At 0.5° the curve for the  $k$  values is made up of two simultaneously occurring effects, as has been noted previously with the sodium halides, the one a linear relationship to urea concentration for Form A

$$k_{0.5^\circ} = 99.530 - 1.70 C_{\text{urea}} \quad (2)$$

and for Form B

$$k_{0.5^\circ} = 64.00 - 1.70 C_{\text{urea}} \quad (2a)$$

(Forms A and B are the respective forms of

TABLE I

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING UREA AT 0.5° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of urea, molal.	Density at 25°	pH	Levo degrees									
				$\lambda$ 6707.86 Å.		$\lambda$ 5892.62 Å.		$\lambda$ 5780.13 Å.		$\lambda$ 5460.73 Å.		$\lambda$ 4358.34 Å.	
				(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]
1	0.00	1.0026	6.04	3.83	248.04	5.14	332.87	5.38	348.41	6.15	398.28	10.86	703.30
2	.50	1.0107	6.22	3.82	245.96	5.13	330.31	5.36	345.13	6.13	394.71	10.83	697.35
3	1.00	1.0189	6.20	3.83	244.11	5.13	326.98	5.37	342.27	6.14	391.35	10.85	691.56
4	1.50	1.0269	6.21	3.79	239.64	5.09	321.84	5.33	337.02	6.09	385.08	10.75	679.73
5	2.00	1.0354	6.21	3.74	234.53	5.02	314.80	5.25	329.22	6.01	376.87	10.60	664.71
6	2.50	1.0437	6.17	3.61	224.58	4.85	301.71	5.07	315.41	5.80	360.82	10.24	637.03
7	3.00	1.0519	6.28	3.36	207.38	4.51	278.37	4.72	291.34	5.39	332.68	9.51	586.97
8	3.50	1.0604	6.38	2.99	183.08	4.02	246.15	4.20	257.12	4.81	294.53	8.48	519.25
9	4.00	1.0691	6.52	2.66	161.54	3.57	216.81	3.74	227.13	4.27	259.32	7.54	457.91
10	4.50	1.0776	6.45	2.46	148.22	3.31	199.43	3.46	208.47	3.96	238.60	6.98	420.56
11	5.00	1.0866	6.59	2.36	141.02	3.18	190.02	3.33	198.98	3.80	227.06	6.70	400.35
12	6.00	1.1037	6.62	2.28	134.12	3.06	180.01	3.20	188.25	3.66	215.31	6.46	380.02
13	7.00	1.1216	6.64	2.24	129.67	3.02	174.83	3.15	182.35	3.60	208.40	6.36	368.18

TABLE II

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING UREA AT 40° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of urea, molal.	Density at 25°	pH	Levo degrees									
				$\lambda$ 6707.86 Å.		$\lambda$ 5892.62 Å.		$\lambda$ 5780.13 Å.		$\lambda$ 5460.73 Å.		$\lambda$ 4358.34 Å.	
				(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]	(a)	[ $\alpha$ ]
1	0.00	1.0026	6.04	1.71	110.74	2.30	148.95	2.41	156.07	2.75	178.09	4.86	314.74
2	.50	1.0107	6.22	1.73	111.39	2.33	150.03	2.44	157.11	2.78	179.00	4.92	316.80
3	1.00	1.0189	6.20	1.76	112.18	2.37	151.06	2.48	158.07	2.83	180.38	5.00	318.69
4	1.50	1.0269	6.21	1.79	113.18	2.40	151.75	2.51	159.34	2.88	182.10	5.07	320.58
5	2.00	1.0354	6.21	1.82	114.13	2.44	153.01	2.55	159.91	2.92	183.11	5.15	322.95
6	2.50	1.0437	6.17	1.84	114.46	2.47	153.66	2.59	161.12	2.96	184.14	5.22	324.73
7	3.00	1.0519	6.28	1.87	115.42	2.52	155.54	2.63	162.33	3.01	185.78	5.31	327.74
8	3.50	1.0604	6.38	1.90	116.34	2.55	156.14	2.67	163.49	3.05	186.76	5.39	330.04
9	4.00	1.0691	6.52	1.93	117.21	2.59	157.29	2.71	164.58	3.10	188.26	5.47	332.20
10	4.50	1.0776	6.45	1.96	118.09	2.63	158.46	2.75	165.69	3.14	189.19	5.54	333.79
11	5.00	1.0866	6.59	1.98	118.32	2.67	159.54	2.79	166.71	3.19	190.62	5.62	335.82
12	6.00	1.1037	6.62	2.05	120.59	2.76	162.36	2.88	169.42	3.29	193.54	5.81	341.79
13	7.00	1.1216	6.64	2.11	122.17	2.84	164.41	2.96	171.35	3.39	196.24	5.98	346.18

gelatin in low urea and high urea concentrations) and a second relationship

$$C_{\text{urea}} = \frac{1}{0.89} \left[ \log \left( \frac{a}{1-a} \right) \right] - \log (1/K) \quad (3)$$

where  $a$  represents the fraction of the gelatin undergoing change as shown by the change in magnitude of the dispersion constants  $k_{0.5}$ . In Table III are given the  $a$  values for the fraction undergoing change and the calculated values obtained for  $\log (1/K)$ . The latter agree well with one another and give a mean value of 3.373. The factor  $1/0.89$  preceding the  $a/(1-a)$  term regulates how rapidly the change takes place from one optically active form to the other.

In its influence on the rotatory dispersion of gelatin at 0.5° urea stands about midway between sodium chloride and bromide. With all of the sodium halides, the product of the constants preceding the logarithmic  $a/(1-a)$  term multiplied by the  $\log (1/K)$  term,  $[k \log (1/K)]$ , gave a constant (2.66); however, the product of these con-

stants for urea ( $0.89 \times 3.37 = 3.00$ ) does not have the same value as for the sodium halides.

TABLE III

ROTATORY DISPERSION CONSTANTS AT 0.5 AND 40°

Soln.	Concn. urea, molal.	$k_{0.5}$	$a$	$\log (1/K)$	$k_{40}$
1	0.00	99.530	..	..	44.521
2	.50	98.681	..	..	44.801
3	1.00	97.832	..	..	45.103
4	1.50	96.220	0.0214	3.3762	45.401
5	2.00	94.107	.0570	3.3711	45.739
6	2.50	90.151	.1415	3.3796	45.975
7	3.00	83.156	.3173	3.3739	46.401
8	3.50	73.519	.5646	3.3733	46.688
9	4.00	64.826	.7853	3.3672	47.025
10	4.50	59.561	.9096	3.3734	47.323
11	5.00	56.727	.9654	3.3735	47.593
12	6.00	53.801	1.000	..	48.394
13	7.00	52.094	1.000	..	49.010

$$k_{40} = 44.521 + x_1 C_{\text{urea}} \text{ where } x_1 = 0.6138$$

$$k_{0.5} = 99.530 - x_2 C_{\text{urea}} \text{ where } x_2 = 1.700 \text{ (Form A)}$$

$$k_{0.5} = 64.00 - x_2 C_{\text{urea}} \text{ where } x_2 = 1.700 \text{ (Form B)}$$

$$\text{mean } \log (1/K) = 3.3735$$

$$k = 0.89 \text{ (const. preceding } a/(1-a) \text{ term)}$$

This indicates that general equation (3) cannot be simplified further to fit all cases although simplification of the equation for similar salts such as the alkali halides appears justified, as we have already shown.

In Table IV are given the various constants obtained at the various wave lengths for the various combinations employed, calculated from the Lucas equation<sup>10</sup> for a system containing two optically active molecular species having unequal dispersion constants. The constancy obtained for a given combination for the five wave lengths used shows that two and only two optically active species of molecule are present, one the original gelatin molecule (probably gelatin ion of the type  $\text{RHC} \begin{matrix} \text{COO}^- \\ \text{NH}_3 \end{matrix}$ ) and the other the molecule after it has undergone the change recorded by the logarithmic equation.

TABLE IV

CALCULATION OF THE LUCAS CONSTANT FOR GELATIN-UREA SYSTEMS CONTAINING TWO OPTICALLY ACTIVE COMPONENTS (0.5°)

Combination <sup>a</sup>	$\lambda$ 6708 Å.	$\lambda$ 5892 Å.	$\lambda$ 5780 Å.	$\lambda$ 5461 Å.	$\lambda$ 4358 Å.
1-2/1-13	0.0176	0.0162	0.0198	0.0188	0.0197
1-3/1-13	.0332	.0373	.0370	.0365	.0350
1-4/1-13	.0710	.0698	.0686	.0695	.0703
1-5/1-13	.114	.114	.116	.113	.115
1-6/1-13	.198	.197	.199	.197	.198
1-7/1-13	.344	.345	.344	.346	.347
1-8/1-13	.549	.549	.550	.546	.549
1-9/1-13	.731	.734	.730	.732	.732
1-10/1-13	.843	.844	.843	.841	.844
1-11/1-13	.904	.904	.900	.902	.904
1-12/1-13	.962	.967	.966	.964	.965

<sup>a</sup> The numbers in this column refer to corresponding soln. no. in Table I.

In Table V we have recorded the rotation and dispersion constant at 0.5° for five different wave lengths, of gelatin which had been treated with 7.0 molal urea solution for a week at 0.5°, after which the solution was placed in collodion tubes and the urea dialyzed out. The dialyzed gelatin solution was then concentrated by freezing out part of the water as ice, was brought to the desired pH with dilute sodium hydroxide solution, the gelatin concentration determined, the polarizing tubes filled and the gelatin allowed to come to equilibrium during a week at 0.5°, at which temperature they were finally read in the polariscope. The average rotatory dispersion constant of the gelatin

(10) Lucas, *Ann. phys.*, [10] 9, 381 (1928); *Trans. Faraday Soc.*, 26, 418 (1930).

going through this cycle of treatment with urea was found to be 99.477 as compared with 99.530 for the original gelatin before treatment. The identity of these constants to one part in 2000 led us to conclude that gelatin suffers no permanent change due to treatment with urea such as is often referred to under the term "denaturation." In the case of gelatin the change is clearly reversible on removing the urea, the same as we have found repeatedly to be the case with neutral salts.

TABLE V

SPECIFIC ROTATION OF GELATIN SOLUTION AT 0.5° AFTER DIALYSIS OF UREA

Gelatin concn. 0.7858 g. per 100 g. soln.; pH = 6.30;  $d = 1.0027$

$\lambda$	( $\alpha$ )	$[\alpha]$	$k_{0.5^\circ}$
6708	3.91	247.56	99.409
5893	5.26	333.04	99.522
5780	5.50	348.23	99.489
5461	6.29	398.25	99.481
4358	11.10	702.80	99.482
Mean			99.477

Although the same general equations express the influence of the dipole ion  $^+\text{NH}_3\text{C}(=\text{NH})\text{O}^-$  on gelatin as was found for the simple halide salts, the gelatin ion changed by urea has a dispersion constant of 64.00 at 0.5° when extrapolated to zero urea concentration as contrasted with a similar value of 46.33 for the gelatin ion when changed by the sodium halides. This total change by urea amounts to exactly two-thirds of the change produced by the sodium halides.

### Summary

The rotatory dispersion of gelatin in urea solutions has been examined at 0.5 and 40° and was found to follow a single-term Drude equation.

At 40° the dispersion constants bear a linear relation to urea concentration,  $k_{40^\circ} = 44.517 + 0.6138 C_{\text{urea}}$ .

The dispersion at 0.5° is the result of two effects, one a linear relation to urea concentration for Form A of  $k_{0.5^\circ} = 99.530 - 1.70 C_{\text{urea}}$ , and for Form B of  $K_{0.5^\circ} = 64.00 - 1.70 C_{\text{urea}}$  and the other a logarithmic function,  $C_{\text{urea}} = \frac{1}{0.89} \left[ \log \left( \frac{a}{1-a} \right) \right] - \log (1/K)$  in which  $\log (1/K)$  equals 3.373. Urea is intermediate in effect on the rotation of gelatin at 0.5°, lying between sodium chloride and bromide. The maximum lowering of the dispersion constant of gelatin by urea is only about two-thirds that produced by the halides of sodium.

After dialyzing out the urea from several of the most concentrated solutions, the rotatory dispersion constant returned to its original value at

0.5°, showing that gelatin had undergone no denaturation by urea.

GENEVA, NEW YORK

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[CONTRIBUTION FROM THE PHYSICS LABORATORIES, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

## Magneto-Optic Rotations of Paramagnetic Ions

BY SAMUEL STEINGISER AND HERBERT HYMAN

The purpose of this investigation was to observe the magneto-optic rotations of dilute solutions of complex iron salts, and to determine the partial Verdet constants. The three salts investigated were potassium ferricyanide, potassium ferrocyanide, and ferric ammonium sulfate. Ferrous ammonium sulfate was also tried, but since it absorbed most of the light in the range of the sodium lamp, accurate measurements could not be made.

### Experimental

**Materials and Apparatus.**—All chemicals were of C. P. grade. Since, in the very dilute solutions used, a relatively large impurity would be necessary to affect the results, no further purification was attempted. The concentrations of the solutions were determined by density measurements. These were made on a chainomatic specific gravity balance, and the concentrations found from tables in the "International Critical Tables."

The source of light, for the values reported, was a General Electric Sodium Lab-Arc,  $\lambda_D = 5893 \text{ \AA}$ . (Earlier preliminary investigations were made using a mercury vapor quartz arc, but this was abandoned in favor of the more universal sodium arc.) Nicol prisms were used as polarizer and analyzer. The angle setting on the scale could be read to 0.1° and estimated to within 0.01° with the aid of a telescope and cross-hair. The Pyrex glass cell, containing the liquid under investigation, was a 21.6-cm. long tube with the ends of optically flat glass fused into the body of the cell. No cement was used on any part of the tube. It was mounted on wooden supports inside the hollow core of a large coil. The coil was 25 cm. in length, formed by winding 2-mm. diameter insulated copper wire in 17 layers of 125 turns each on a copper cylinder. The coil extended sufficiently beyond the tube to eliminate any distortion of the magnetic field due to edge effects.

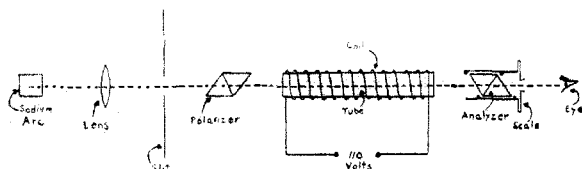


Fig. 1.—Schematic diagram of apparatus.

The apparatus was calibrated using carbon disulfide and distilled water over a range of currents as can be seen from the data. The Verdet constants for these two liquids were

obtained from the "International Critical Tables." In order to facilitate calculations of the Verdet constants of the solutions under investigation, a conversion factor was found, as shown, equal to 0.0399 Verdet unit/deg./amp.

**Measurements.**—The values reported are the average of nine independent measurements with the field off, recorded in the tables below as  $N^0$ , nine with the field causing rotation clockwise,  $R^0$ , and finally nine with the field causing rotation counterclockwise,  $L^0$ . Altogether twenty-seven readings were taken for each solution and the average with its mean deviation calculated.

Although the partial Verdet rotations of some of the salts are in opposite directions to that of water, the actual rotations, in all cases measured, were in the same direction, due to the rather dilute solutions used. The partial Verdet constant is defined so that

$$N_1 V_1 + N_2 V_2 = V$$

where  $N_2$  and  $N_1$  are the mole fractions of the solute and solvent, respectively,  $V$  is the observed Verdet constant for the solution, and  $V_2$  and  $V_1$  are the partial Verdet constants of the solute and solvent. This equation is by definition exact, but in using it to determine  $V_2$ , it is necessary to make the assumption that  $V_1$  equals the Verdet constant of pure water. While this undoubtedly is not true in concentrated solutions, it is probably true within the limit of experimental error in the solutions used in these measurements.  $V_2$  is not necessarily the Verdet constant of the pure salt and should not be regarded as such, but is the Verdet constant of the salt in the solution of definite molality. There is considerable evidence to show that it may be regarded as constant over a considerable range of concentrations.

The agreement between the two standardizing substances is thus seen to be very good.

The factor for converting the rotation deg./amp. into Verdet units is 0.0399 Verdet unit/deg./amp.